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FAILURE CRITERIA FOR PARTICULATE REINFORCED GLASSY POLYMERS

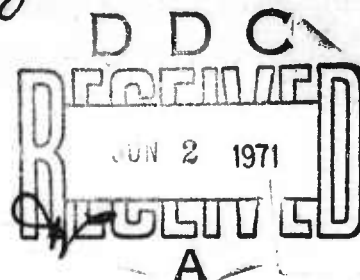
BY
L. NICOLAIS AND A. T. DIBENEDETTO

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13. ABSTRACT

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It has been shown that the addition of particulate filler to a polyphenylene oxide polymer increases the rate of nucleation of crazes relative to their rate of growth, thereby promoting a greater tendency for macroscopic yielding. It was also shown that the composite stress-strain behavior can be described in terms of constituent properties and volume fraction of filler.

14.

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FAILURE CRITERIA FOR PARTICULATE REINFORCED GLASSY POLYMERS

BY

L. NICOLAIS AND A.T. DICENEDDETTO

APRIL 1971

MONSANTO/WASHINGTON UNIVERSITY ASSOCIATION
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800 NORTH LINDBERGH BOULEVARD
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FOREWORD

The research reported herein was conducted by the staff of Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl (Phone 314-694-4721).

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FAILURE CRITERIA FOR PARTICULATE REINFORCED GLASSY POLYMERS

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ABSTRACT

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*On leave from the Laboratorio di Ricerca su Tecnologia dei Polimeri e Reologia del C.N.R. Napoli, Italy.

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INTRODUCTION

At temperatures below the primary glass transition, most organic polymers exhibit either brittle or ductile failure, depending upon the load and temperature history imposed on the material. When ductile, these polymers are tough and resistant to impact and when brittle they are not. Polyblending with finely dispersed particles sometimes results in large increases in toughness, while polyblending with coarse rigid particles sometimes results in increased brittleness.

The difficulty in describing the stress-strain behavior is complicated by many factors, of which the formation and growth of defects during loading is perhaps the most important. It is well known that the presence of stress inhomogeneities and/or finely dispersed second phases can induce crazes, cold flow and a multitude of interacting cracks. In a previous paper (1) the authors presented a general theory of nucleation and growth of submicroscopic defects to account for the irreversible deformation of a polymeric glass. It is the purpose of this paper to use this theory to predict the stress-strain behavior of particulate reinforced glasses.

THEORY

The straining of a polymeric glass results in a volume change that is the sum of an elastic recoverable change associated with the compressibility of the material and an

irreversible non-linear change associated with microcavitation within the solid (2). In many of the polymeric glasses, the microcavitation develops through the formation of crazes (3). Crazes are structured regions analogous to that of a porous sponge, in which the cell walls are highly drawn (4). These porous regions may be thought of as aggregates of microscopic cavities, which concentrate stress in a manner similar to a true crack. In any case, they lead to catastrophic failure through either a general yielding of the material or a brittle fracture (5-6).

In an unfilled polymeric glass, a unidirectional tensile load will cause crazes to nucleate and grow perpendicular to the direction of loading. The presence of a particle in the polymeric matrix causes stress concentrations around the particle, which enhance the rate of craze formation (6). Under certain conditions (in either of the above mentioned cases) the regions of crazing overlap and coalesce to form a nearly continuous zone of crazed material which ultimately leads to a general macroscopic yielding of the solid. This condition can be observed experimentally by the development of necking and optical birefringence, or less precisely by the appearance of an apparent maximum in the engineering stress-strain curve. Under other conditions, these crazes grow to a greater length than can be tolerated by the material and the craze rapidly changes to a macroscopic crack which propagates catastrophically, causing failure in a brittle manner.

An analytic model for these phenomena have been presented by the authors (1). It was assumed that the isothermal rate of formation of microcavities within the crazed volume, $(\frac{dV_f}{dt})_T$, could be obtained from the product of nucleation and growth processes.

The final result was given as

$$\begin{aligned} \left(\frac{dV_f}{dt} \right)_T &= \beta_o N(t) \left(\frac{dG}{dt} \right) \\ &= B(T) \sinh \frac{\sigma}{\sigma^*} \int_0^t \sinh \frac{(n-1)\sigma}{\sigma^*} dt \end{aligned} \quad (1)$$

where $N(t)$ is the number of nucleated crazes at time t , (dG/dt) is the average rate of growth of a craze site, σ^* and $\sigma^*/(n-1)$ are characteristic stress constants for the growth and nucleation processes respectively, β_o is a porosity factor for the craze and where

$$B(T) = \beta_o N_o G_o \exp - \frac{(\Delta E_N + \Delta E_G)}{RT} \quad (2)$$

The quantities ΔE_N and ΔE_G are activation energies for the nucleation and growth processes respectively and $(\beta_o N_o G_o)$ is a constant.

The total strain was then expressed as the sum of a recoverable elastic strain σ/E_s and an irrecoverable strain caused by the additional volume created by the microcavities in the crazed regions

$$\begin{aligned} \epsilon &= \epsilon_s + \epsilon_p \\ &= \sigma/E_s + \frac{V_f(t)}{(1-2\mu)} \end{aligned} \quad (3)$$

where σ is the stress, E_s is the initial elastic modulus, μ is the Poisson ratio and $V_f(t)$ is the microvoid volume obtained by integration of equation (1).

Equation (3) gives the relationship between stress, strain, temperature and time.

The failure criterion was established by assuming that a certain critical amount of microcavitation $V_f(t_y) = b(T_m - T)$ was required to induce macroscopic yielding in the material. It was found experimentally that this quantity was a linear function of temperature,

independent of strain rate, where (b) is a constant and T_m is the maximum temperature at which craze sites can nucleate. It was also assumed that the criterion for brittle failure is determined by a critical flaw length l_c^* that is primarily a function of temperature and flow density. Whether the material yields before brittle fracture depends upon whether sufficient microvoid volume is developed before reaching the critical flaw size. This depends upon the relative rates of nucleation and growth.

It was shown that the model quantitatively describes the mechanical behavior of polyphenylene oxide and that by using stress-strain data at constant rate of loading, one can predict creep behavior.

EXPERIMENTAL

Composites of polyphenylene oxide and glass microspheres were prepared by dry-mixing the components, compression molding at 285°C and then slowly cooling the mold to room temperature. The polyphenylene oxide was General Electric's Grade 631-III with a glass transition temperature of 210°C and a Poisson's ratio of 0.35. It was supplied as a 20-400 mesh powder and was dried at 125°C and 29.9 inches of vacuum for 8-10 hours prior to compression molding. The glass microbeads were from Cataphote Company and had a size range of 1-30 microns, a density of 2.54 g/cc and a Poisson ratio of 0.25. Prior to use they were magnetically cleaned of iron particles present in the as-received material. The beads were used in an unsized condition with no surface treatment. Materials containing about 10%, 25% and 42% by volume filler were studied. All samples were annealed below T_g to minimize molding stresses. Standard ASTM tensile tests were carried out on an Instron testing machine at temperatures ranging from 34°C to 140°C and at strain rates of 0.00526 to 0.526 in/in-min.

A summary of the yield stress data at constant strain rate is shown in Figure 1. Time-temperature superpositioning at a reference temperature of 34°C (7) was used to condense the data. The shift factor α_T for the abscissa was independent of filler concentration and identical to that for the unfilled polymer:

$$\log_{10} \alpha_T = \frac{8750}{T} - 28 \quad (4)$$

where T is the temperature in degrees Kelvin.

All of the data in Figure 1 can be superimposed to a single curve (8) by shifting along the ordinate by a factor of $(1 - 1.21\phi_f^{2/3})$, as illustrated in Figure 2. Thus, at constant reduced rate of strain ($\dot{\epsilon} \alpha_T$) the yield strength of the composite is given by:

$$(\sigma_{yc})_{\dot{\epsilon} \alpha_T} = (\sigma_{yo})_{\dot{\epsilon} \alpha_T} (1 - 1.21\phi_f^{2/3}) \quad (5)$$

where σ_{yo} is the yield strength of the unfilled material and ϕ_f is the volume fraction of filler.

It was shown previously (1) that the yield strength of the unfilled polymer is given by:

$$\sigma_{yo} = \frac{\sigma_o^*}{n} \left[\frac{1}{n} \frac{4 b (T_m - T) (n - 1) n E_s^2}{B(T) \sigma_o^{*2}} + 2 \ln r_o \right] \quad (6)$$

where E_s is the initial polymer modulus of 3×10^5 psi, $E_s r_o = \dot{\sigma}$ is the rate of stressing in psi/min, $b = 3.09 \times 10^{-5} \text{ } ^\circ\text{K}^{-1}$, $T_m = 525 \text{ } ^\circ\text{K}$, $\sigma_o^* = 334$ psi, $n = 2.3$, $\Delta E_N = 41,700$ cal/g-mole, $\Delta E_G = 32,300$ cal/g mole and $\beta_o N_o G_o = 2 \times 10^{20}$.

From Figure 2 it is clear that the yield strength of the composite is given by:

$$\sigma_{yc} = \left[\ln \frac{4b (T_m - T) (n-1) n E_c^2}{B_c(T) \sigma_c^{*2}} + 2 \ln r_o \right] \frac{\sigma_o^*}{n} \left(1 - 1.21 \phi_f^{2/3} \right) \quad (7)$$

where the subscript c refers to a composite property and the logarithmic argument is constant and equal to that given by equation (6) for the unfilled polymer.

In order to predict the creep behavior of the composites it is necessary to define all of the parameters of the model for the composite materials. In light of the time-temperature superpositioning expressed in equation (4), it is reasonable to assume that the criterion for yielding (and therefore b and T_m) and the thermal activation energies ΔE_N and ΔE_G are properties of the polymer and independent of filler concentration. The initial elastic modulus of the particulate composite E_c can be expressed as a function of concentration by the well known Kerner equation (9) as:

$$E_c = E_s \frac{1 + A C \phi_f}{1 - C \phi_f} \quad (8)$$

where $A = \frac{7 - 5 \mu_p}{8 - 10 \mu_p} = 1.17$ and

$$C = \frac{E_f/E_p - 1}{E_f/E_p + A} = 0.92 \text{ for this polymer.}$$

In order to satisfy the yield behavior expressed in equations (5) to (7) one can assume that the parameter n is a constant and write the characteristic stress constant σ_c^* and the quantity $B_c(T)$ as functions of the concentration:

$$\sigma_c^* = \sigma_o^* (1 - 1.21 \phi_f^{2/3}) \quad (9)$$

$$B_c(T) = \frac{B_o(T) (1 + AC\phi_f)^2}{\left(1 - 1.21 \phi_f^{2/3}\right)^2 \left(1 - C\phi_f\right)^2} \quad (10)$$

Thus, all composite parameters are expressed in terms of constituent properties and filler concentration and the stress-strain behavior of the composite can be deduced from the unfilled polymer behavior.

A sensitive test of the theory is to use the parameters calculated from the stress-strain curves to predict a-priori the irreversible deformation and time to yield under a constant load σ_o (i.e. the creep behavior).

One can express the irreversible deformation as (1):

$$(\epsilon_t - \epsilon_o) = \frac{B_o(T) (1 + AC\phi_f)^2 \sinh \frac{n \sigma_o}{\sigma_o^* (1 - 1.21 \phi_f^{2/3})}}{2 (1 - 1.21 \phi_f^{2/3})^2 (1 - C\phi_f)^2 (1 - 2\mu_c)} t^2 \quad (11)$$

and the time to yield as:

$$t_y = \left\{ \frac{2b (T_m - T) (1 - 1.21 \phi_f^{2/3})^2 (1 - C\phi_f)^2}{B_o(T) (1 + AC\phi_f)^2 \sinh \frac{n \sigma_o}{\sigma_o^* (1 - 1.21 \phi_f^{2/3})}} \right\}^{1/2} \quad (12)$$

where the Poisson ratio of the composite is a volume fraction average of the Poisson ratios of the constituents ($\mu_{\text{glass}} = 0.25$ $\mu_{\text{PPO}} = 0.35$).

Equation 11 is plotted in Figures 3 and 4 and equation 12 is plotted in Figures 5 and 6 for composites containing 10% and 25% by volume filler. The deformation versus time plots were obtained from creep-recovery experiments by keeping the materials at a constant load for a fixed period of time and then removing the load to permit

recovery. The residual deformation at the end of recovery was considered irreversible. Time to yield was determined by observing the time required at a constant load to cause cold drawing of the specimen. The agreement with theoretical predictions is within the experimental error in all cases.

Since both the measured stress and the volume fraction of filler appear in exponential terms in equations 12 and 13, the prediction is very sensitive to these quantities. For example at 10% by volume and a load of 5800 psi, an increase of either 0.5% by volume or 80 psi stress level will increase the irreversible deformation at a given time by nearly 200% and will decrease the time to yield by nearly 50%. Obviously, extreme precision is required in these measurements to provide reasonable predictions. Similar errors for the 42% by volume composite correspond to factors of about 8 in deformation and 3 in the time to yield. Within the normal precision of the experiment it therefore becomes nearly impossible to predict the creep behavior of the 42% by volume composites with any degree of certainty. For this reason, creep experiments are reported only for the 10% and 25% composites.

Since the composite materials were opaque, it was not possible to measure the average craze size as a function of time and temperature. For all conditions studied, however, ductile yielding prevailed, indicating that critical flaw sizes were never reached. This is contrary to the behavior of the unfilled polymer which exhibits brittle failure at many of the test conditions. Thus at these strain rates the filler reduces the sensitivity of the material to flaws by inducing microscopic yielding over a wider range of conditions. In terms of the proposed model, the lowering of the characteristic stress parameter σ^* causes a greater increase in the craze nucleation rate than in the growth rate, thereby causing the formation of a greater number of smaller crazes per unit

volume and per unit of time.

CONCLUDING REMARKS

A theory for predicting the stress-strain behavior of glassy polymeric solids to either the point of brittle failure or the point of macroscopic yielding has been presented. The process of irreversible deformation is assumed to be a combination of nucleation of sub-microscopic defects at stress inhomogeneities and their subsequent growth to macroscopic dimensions. The nature of the failure is determined by a competition between the dilational strain associated with the microcavitation, causing the stress-strain curve to deflect from linearity, and the linear growth of stress concentrators that are potential sources for brittle failure. Yielding occurs when there is sufficient microcavitation prior to the formation of critical flaws.

It has been shown that the addition of particulate filler to a polyphenylene oxide polymer increases the rate of nucleation of crazes relative to their rate of growth, thereby promoting a greater tendency for macroscopic yielding. Further, it was shown that the composite stress-strain behavior can be described in terms of constituent properties and volume fraction of filler.

It is tempting to extrapolate these results to describe qualitatively the toughness and impact properties of these materials. This is not always reliable, however, since the modulus of toughness depends on the total area under the stress-strain curve. The model characterizes behavior only to the point of yielding. Beyond this point the material becomes highly anisotropic and the nucleation, growth and coalescence of crazes cannot be described simply. Indeed, post yielding phenomena in the filled materials might be quite different than in the unfilled material.

Interpretation of impact properties is even more difficult. Very high rates of loading at a stress inhomogeneity (e.g. at a notch tip) will lead to a very high rate of nucleation of microcavities and therefore a very high local density of defects. These are likely to coalesce and grow into microcracks in a different manner than the crazes formed at lower strain rates. The experimental evidence indicates that as the strain rate increases to the range common in impact tests, the microcavitation becomes highly localized and the tendency toward brittle failure again dominates. In terms of the above model, the critical defect size l_c^* must be considerably smaller at high deformation rate.

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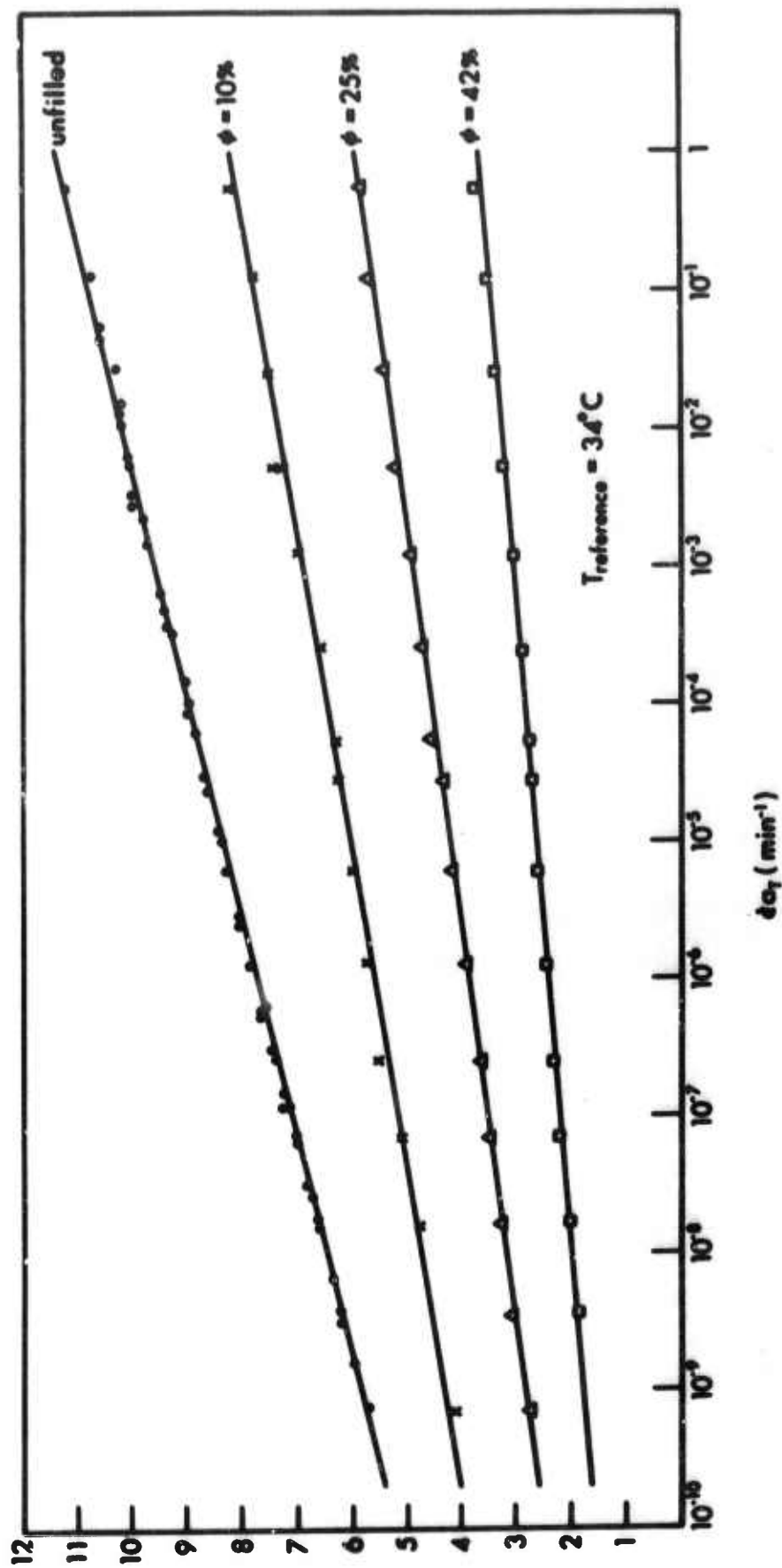


Figure 1. Effect of strain rate on yield stress for different concentration of glass beads.

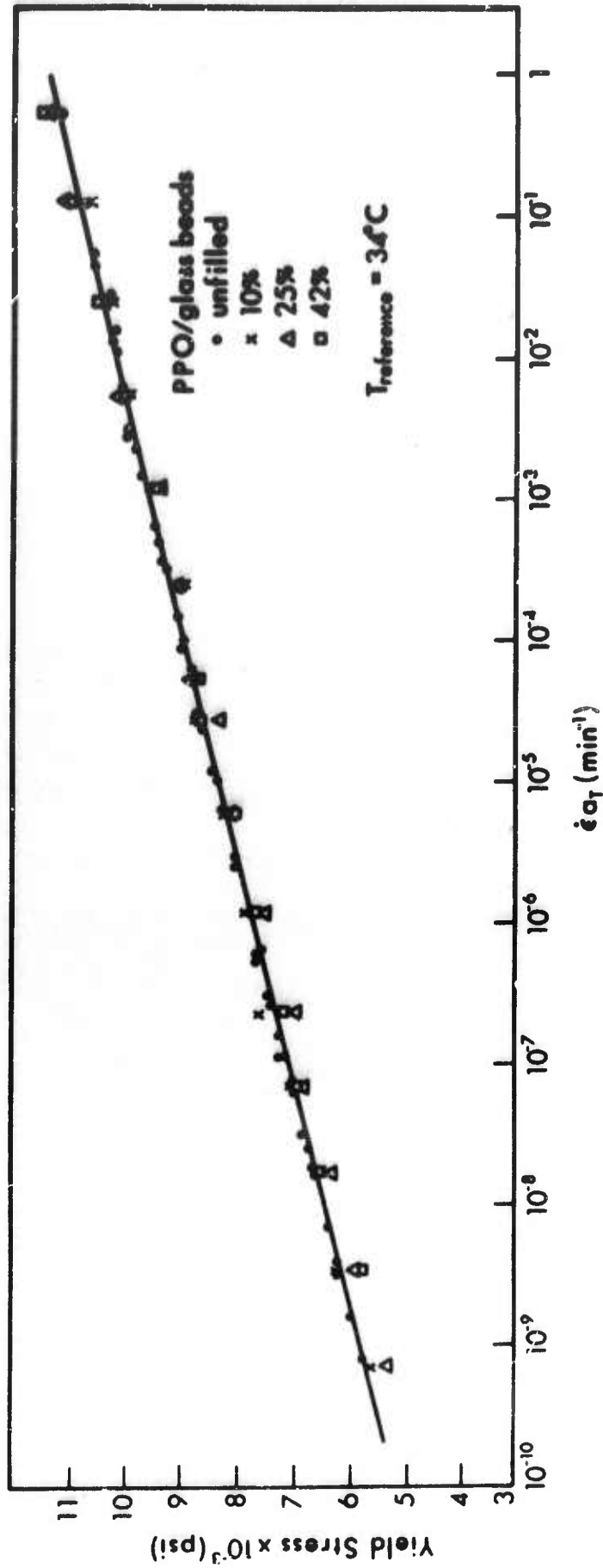


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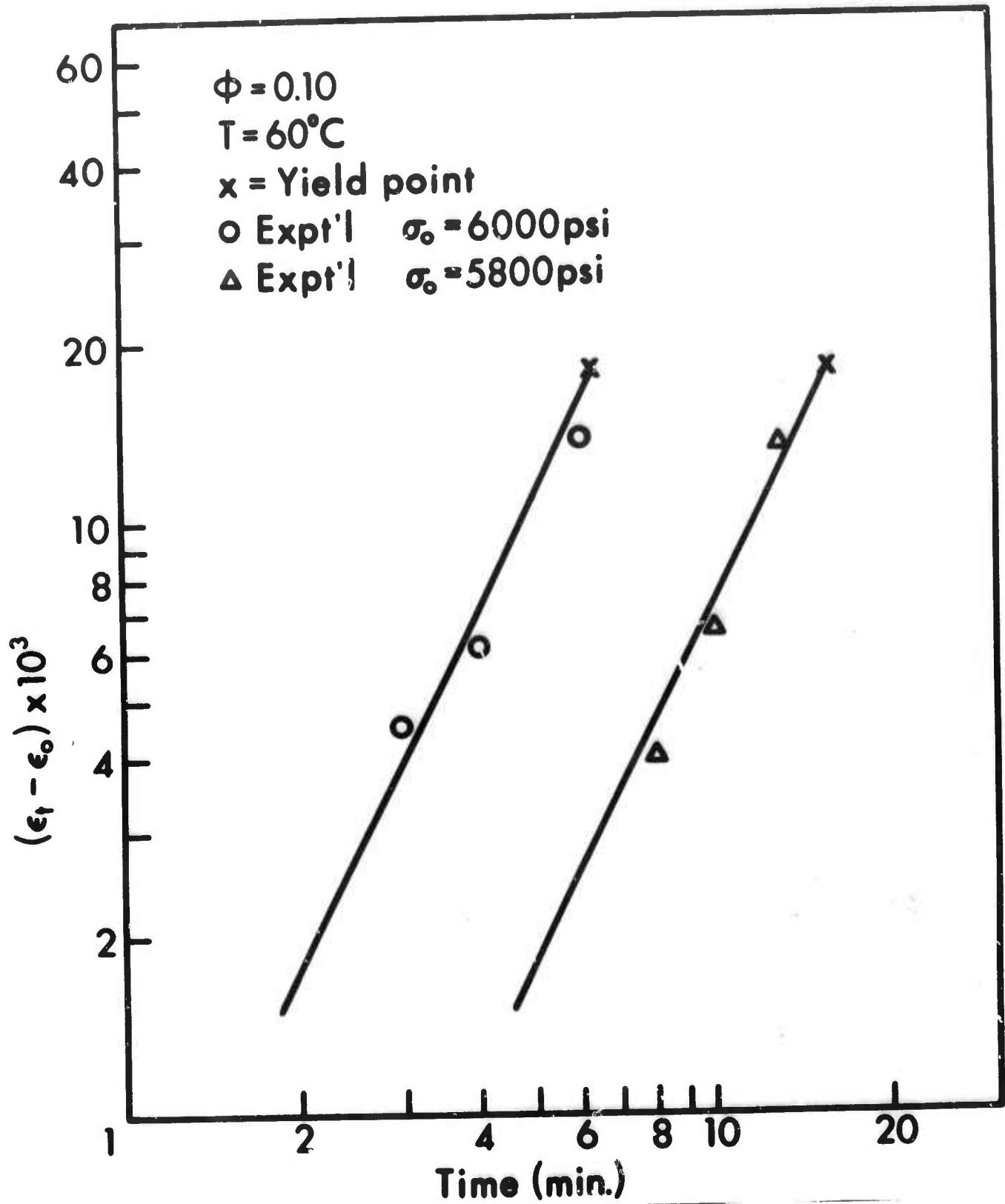


Figure 3. Non-recoverable deformation in creep as a function of time.
 $\phi = 0.10$.

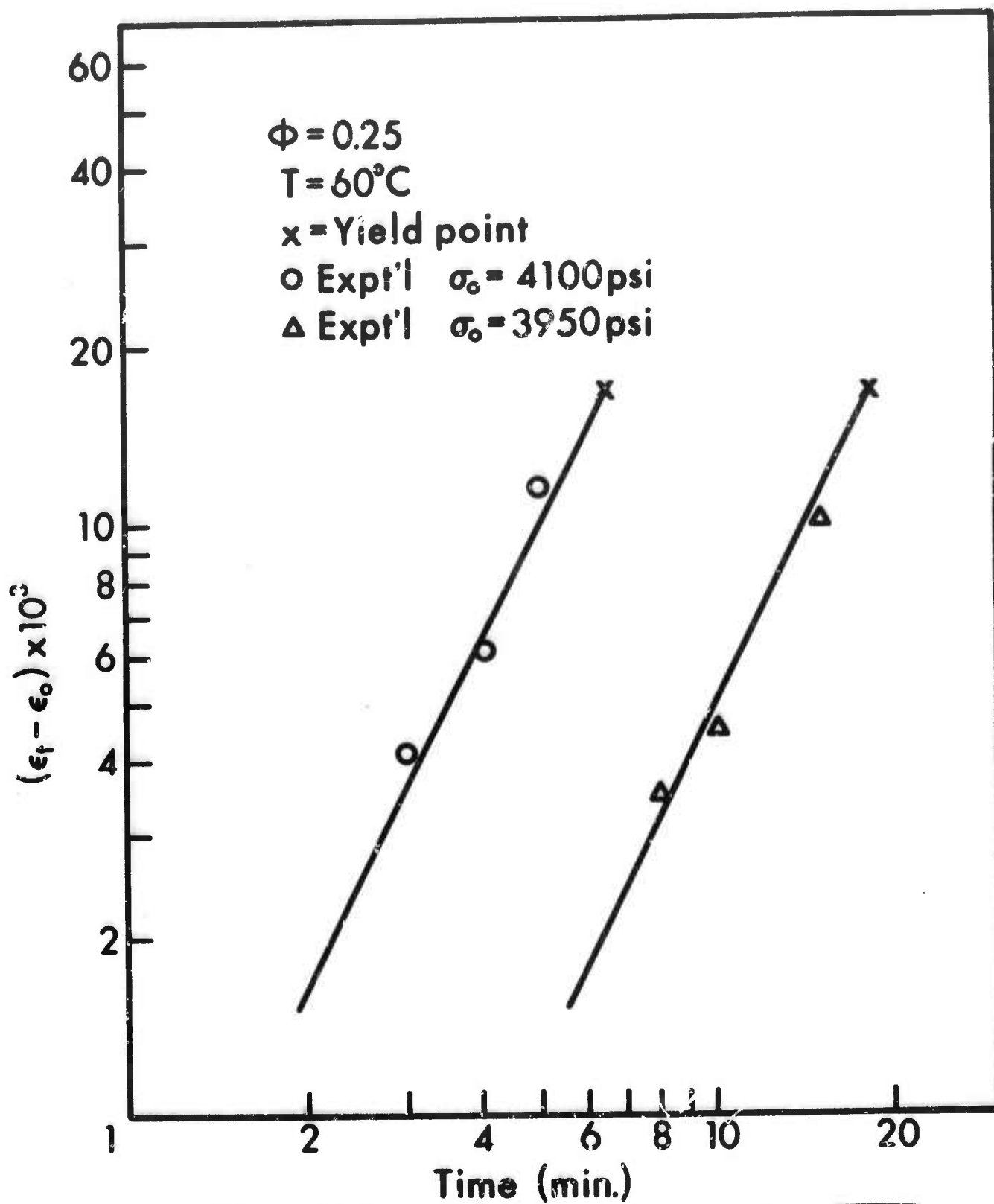


Figure 4. Non-recoverable deformation in creep as a function of time.
 $\phi = 0.25$.

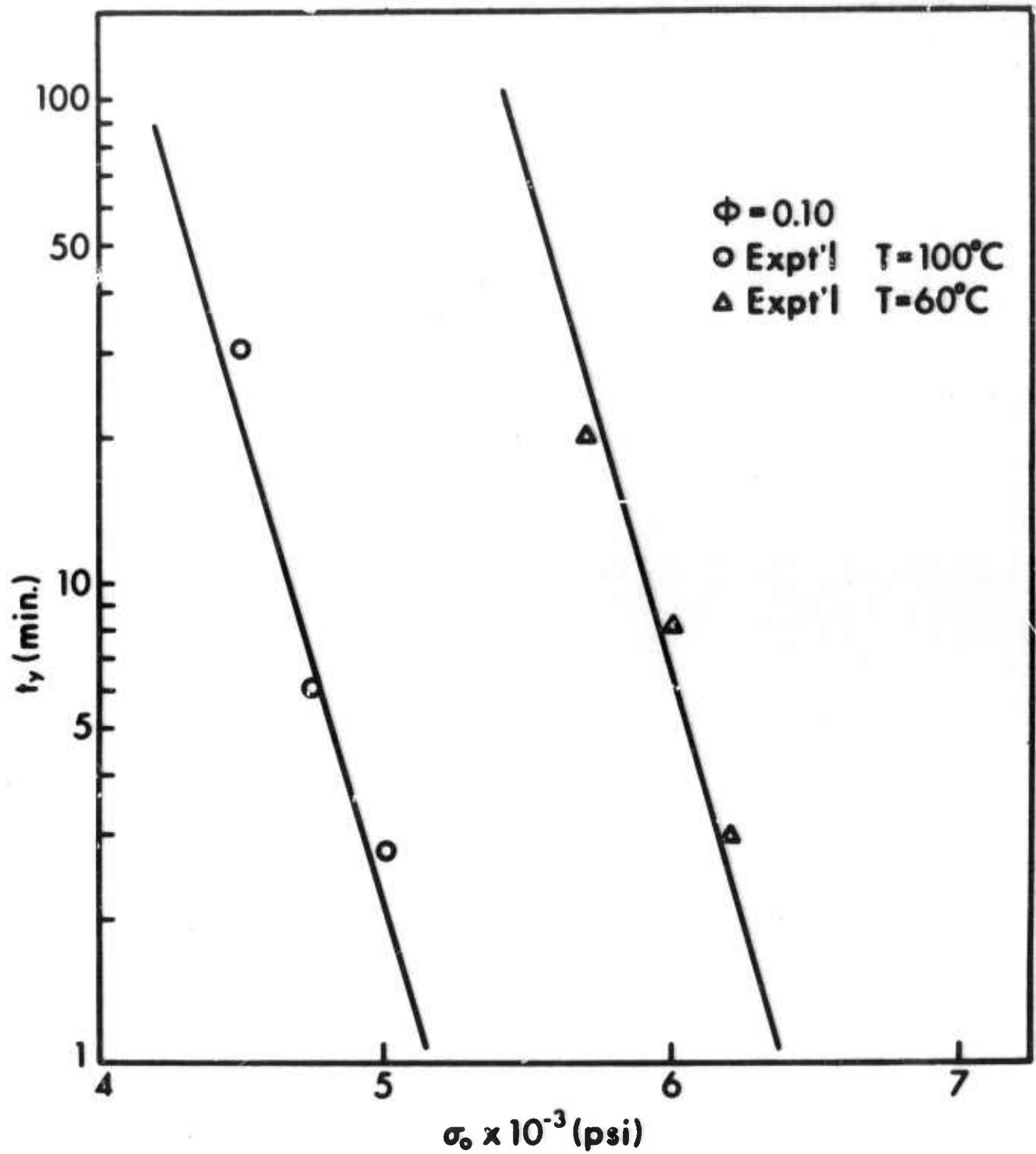


Figure 5. Time to yield under constant load. $\phi = 0.10$.

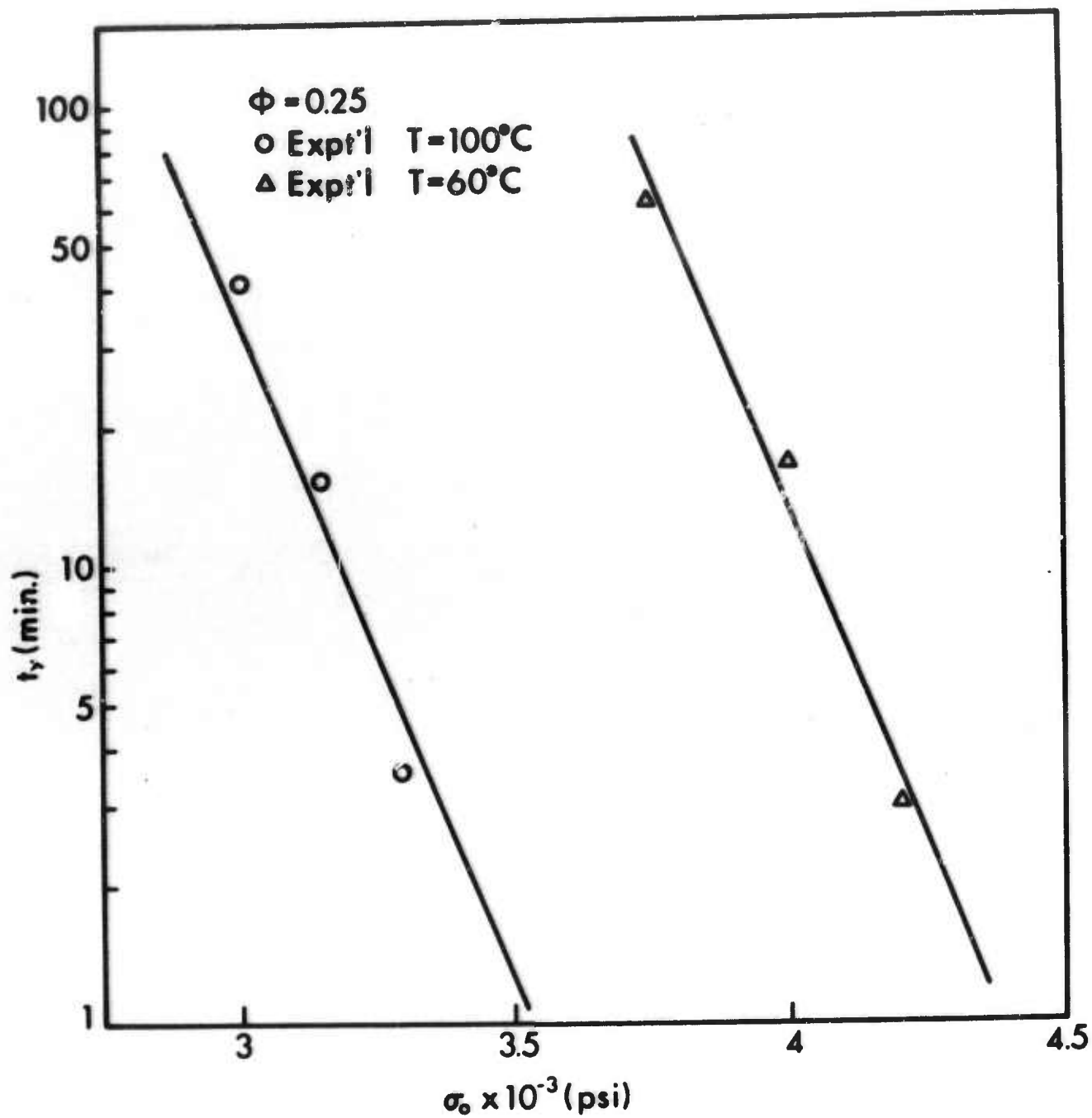


Figure 6. Time to yield under constant load. $\phi = 0.25$.